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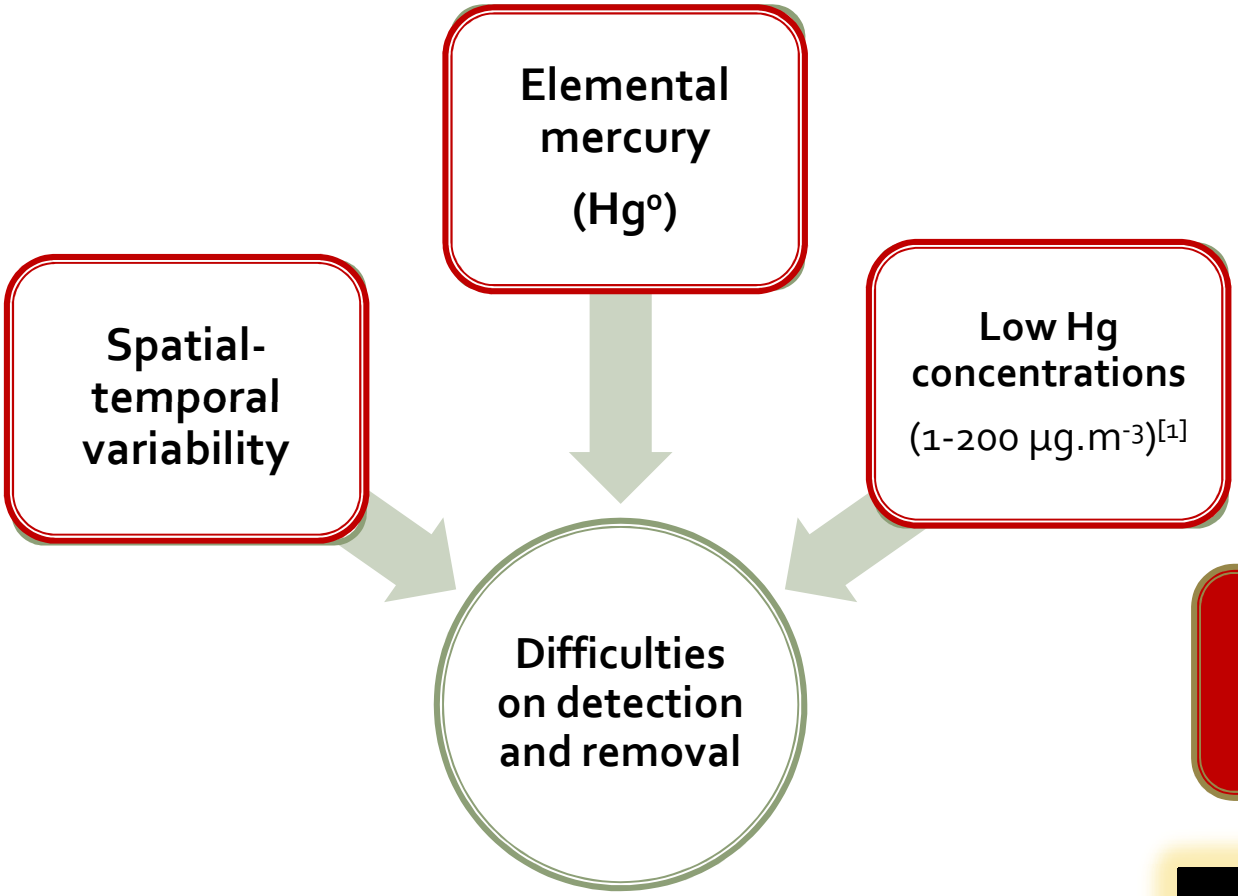
USE OF SULFIDE/PHOSPHATE BASED SORBENTS FOR MERCURY REMOVAL FROM NATURAL GAS: A FOCUS ON Hg STABILIZATION



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Amanda G. Oliveira, Neuman S. Resende,
Vera M. M. Salim, Frederico W. Tavares



Mercury in Natural Gas (NG)



Hg REMOVAL FROM NG

WHY is this important?

[1] Shafawi, A., Ebdon, L., Foulkes, M. *et al.* (1999)*The Analyst*, **124**, 185.

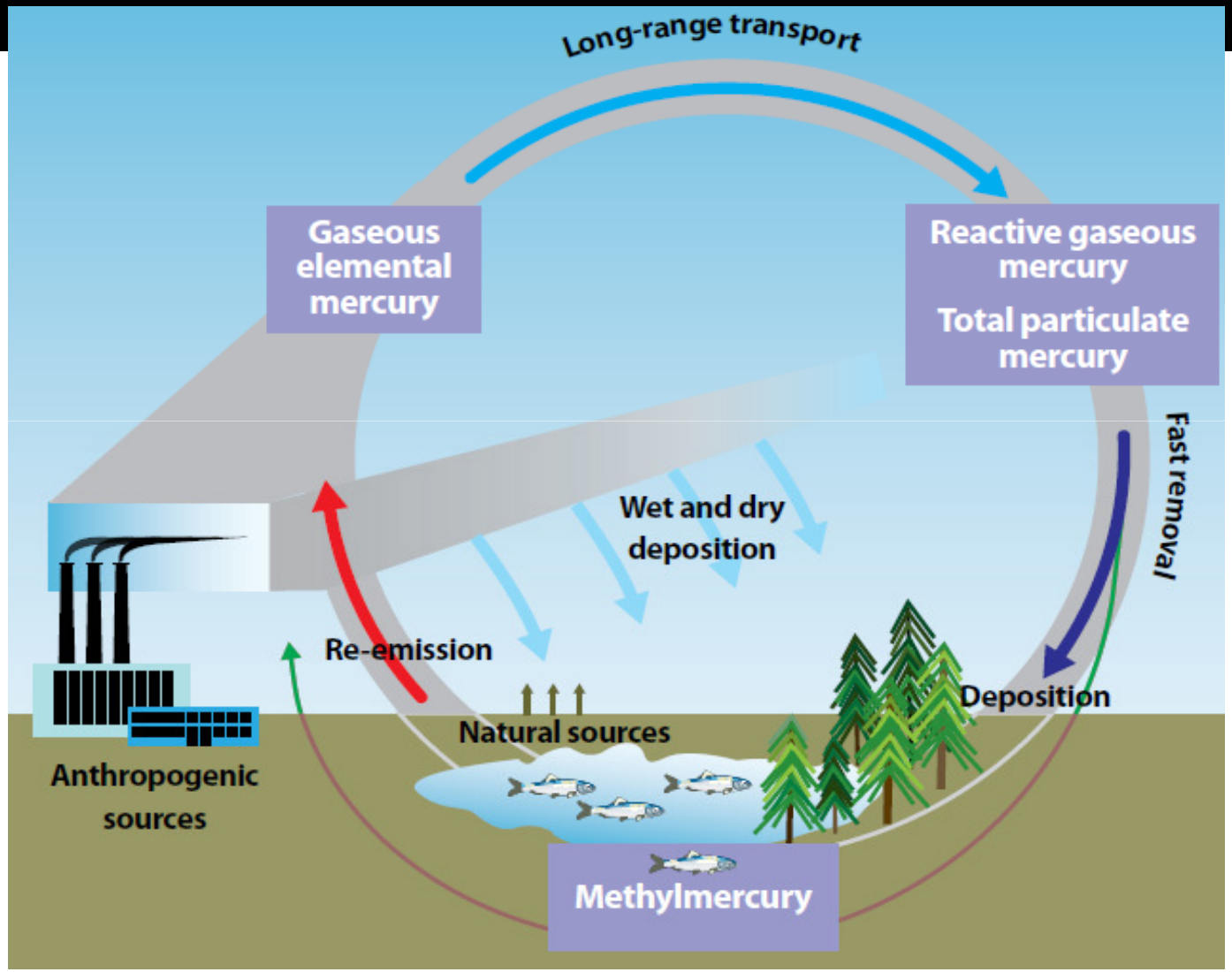
Hg – NG: Problems in NG plants

- ✓Corrosion of Al-structures
- ✓Accidents
- ✓Condensation
- ✓Shutdowns
- ✓Occupational exposure
- ✓Mercury emissions



[2] Pawel, S.J., Manneschmidt E.T. (2003) *Journal of Nuclear Materials*, **318**, 355

Environmental Cycle of Mercury

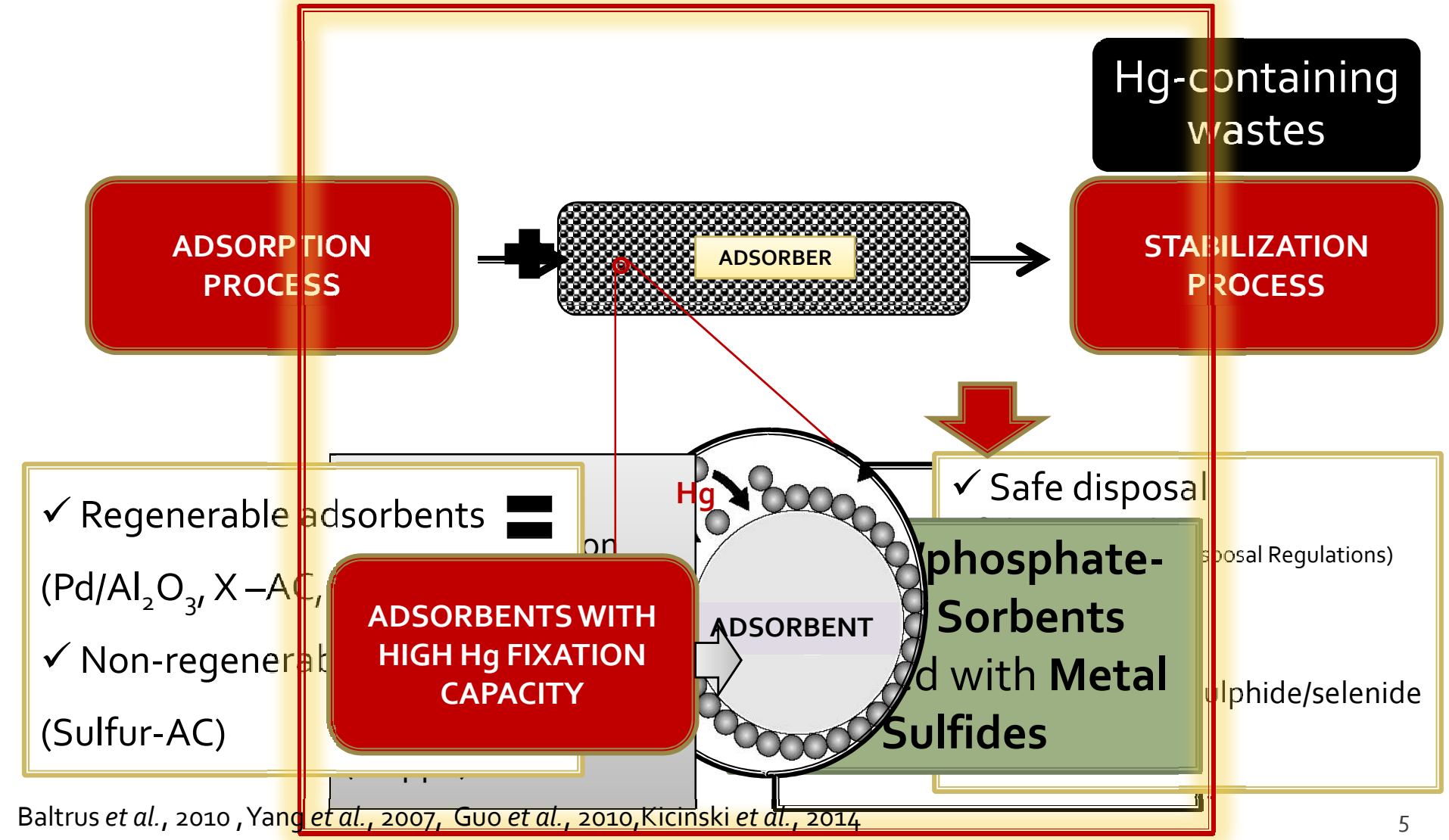


- ✓ Toxicity
- ✓ Bioaccumulation
- ✓ Global pollution

- ✓ Rigid environmental laws

[3] UNEP. UNITED NATIONS ENVIRONMENT PROGRAMME, 2008, *The Global Atmospheric Mercury Assessment: Sources, Emissions and Transport*. UNEP-Chemicals, Geneva, Switzerland.

Hg Removal and Stabilization

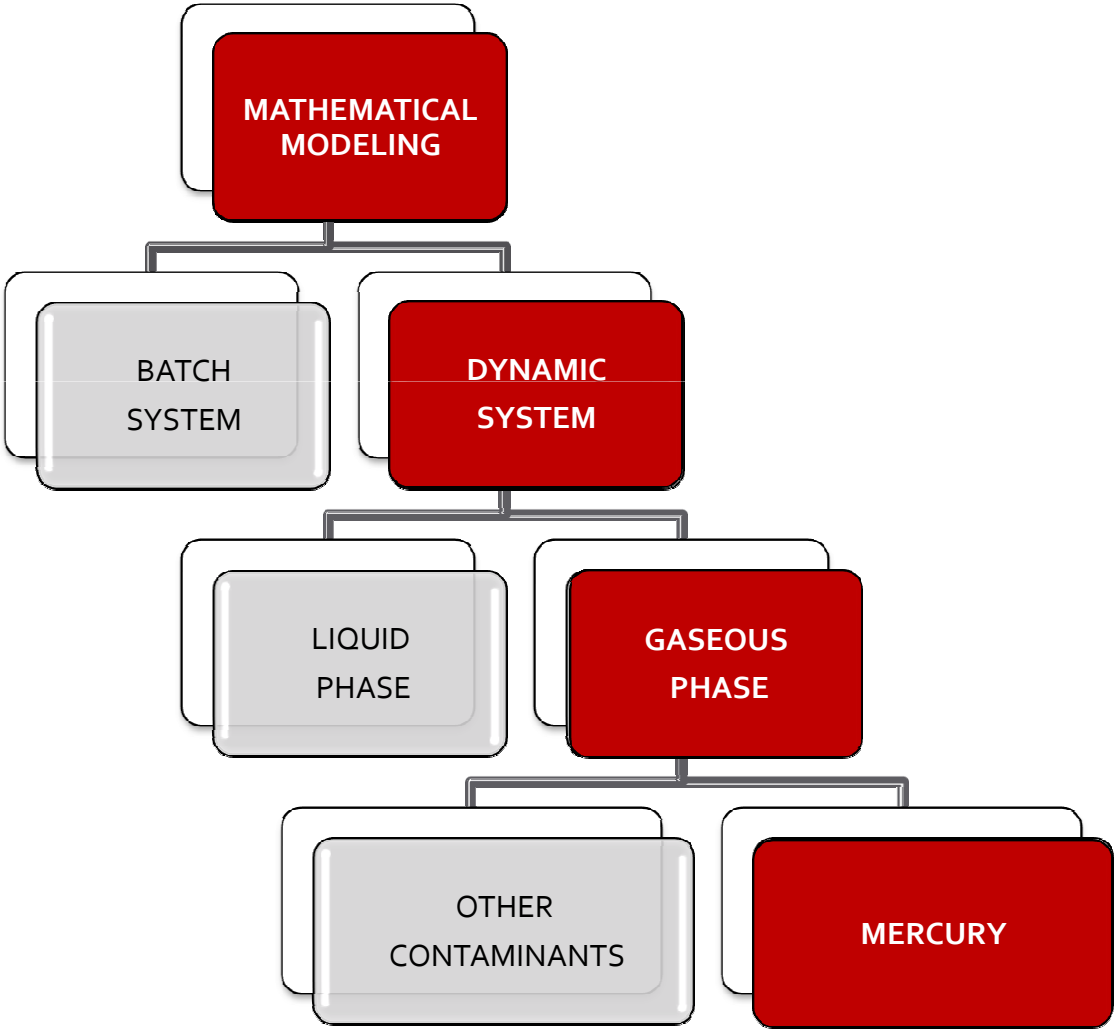


Baltrus *et al.*, 2010 , Yang *et al.*, 2007, Guo *et al.*, 2010,Kicinski *et al.*, 2014

Research topics

- ✓ Development of modified HAp-sorbents to Hg removal from NG;
- ✓ Physical-chemical characterization of sorbents;
- ✓ **Study of Hg removal capacity adsorption tests;**
- ✓ **Investigation of removal mechanisms by mathematical modeling;**
- ✓ Study of stabilization capacity by lixiviation and thermal stability tests;
- ✓ Study of sorbent structures by experimental and computational techniques.

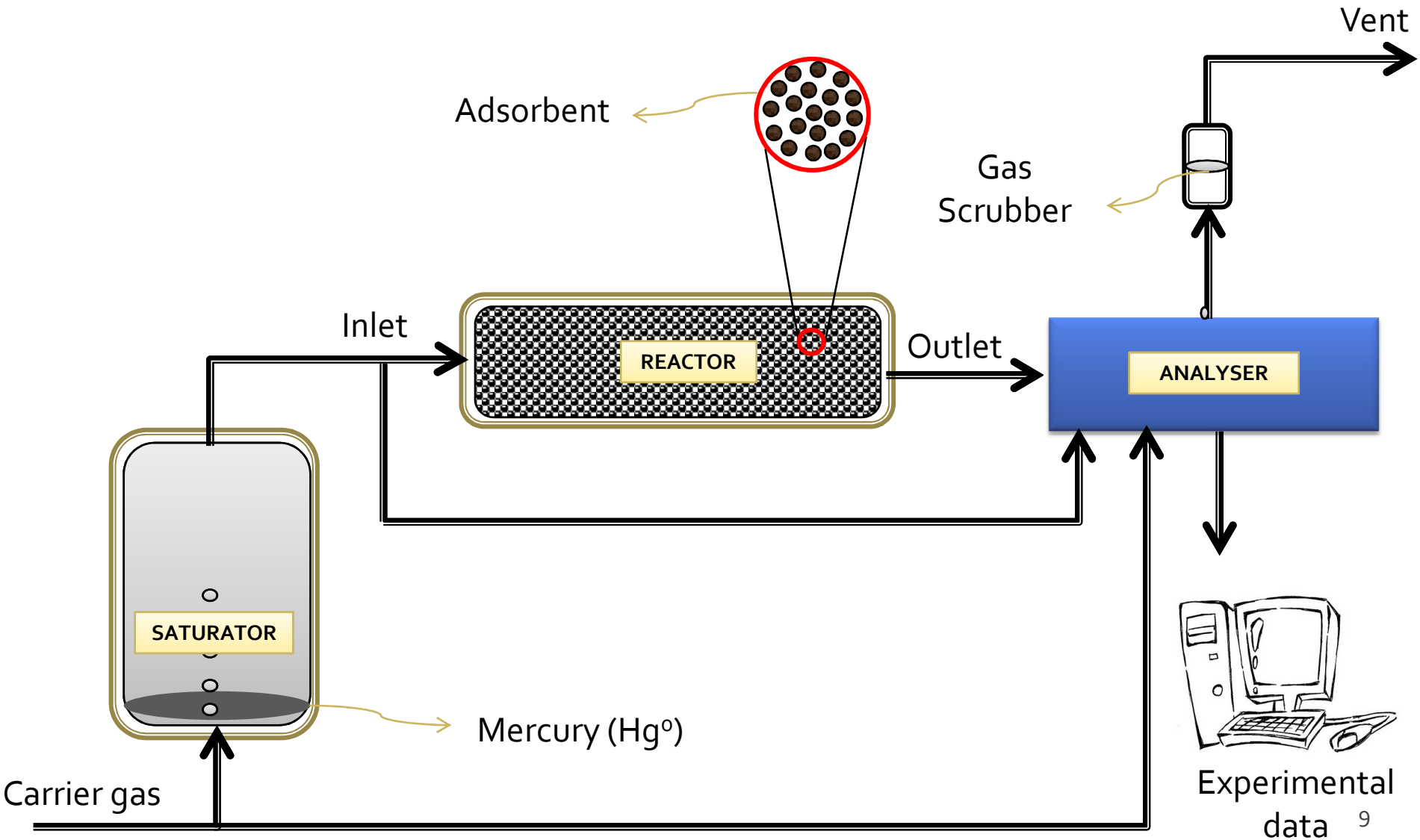
Mathematical Models for Adsorption Processes



Dynamic System

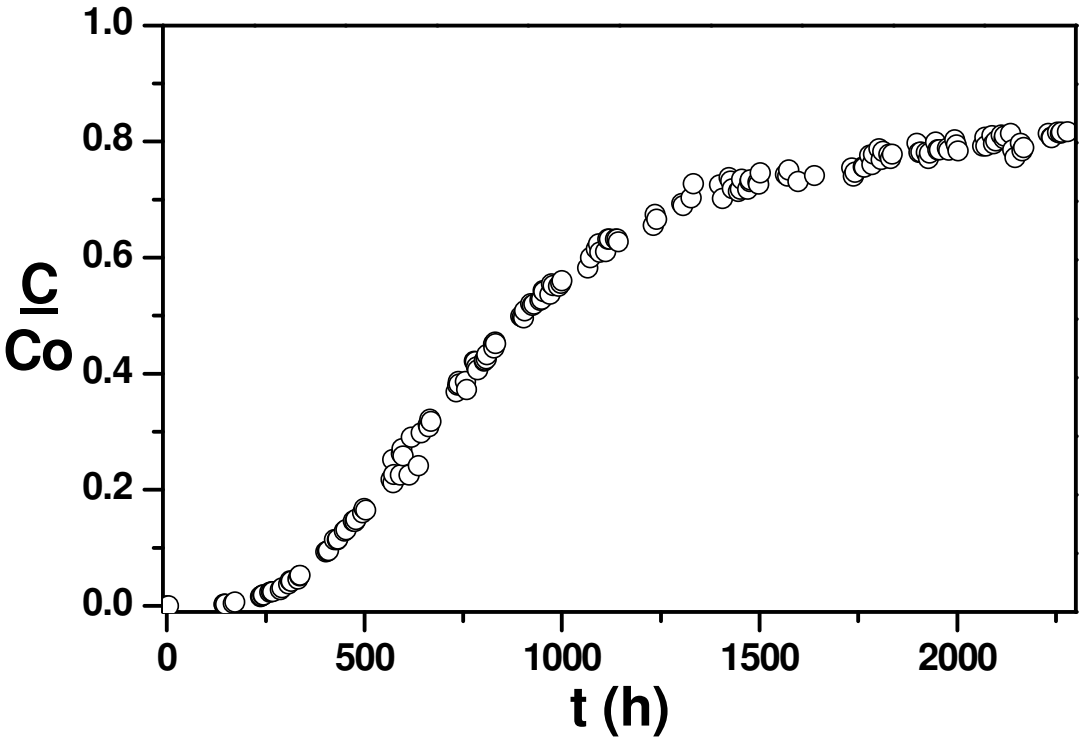


Dynamic System



Adsorption Tests

BREAKTHROGH CURVES



SORBENT

Hydroxyapatite (HAp)

$M_{10-z}(HPO_4)_z(PO_4)_{6-z}(OH)_{2-z}$

M:Ca, Cu, Cd, Zn…

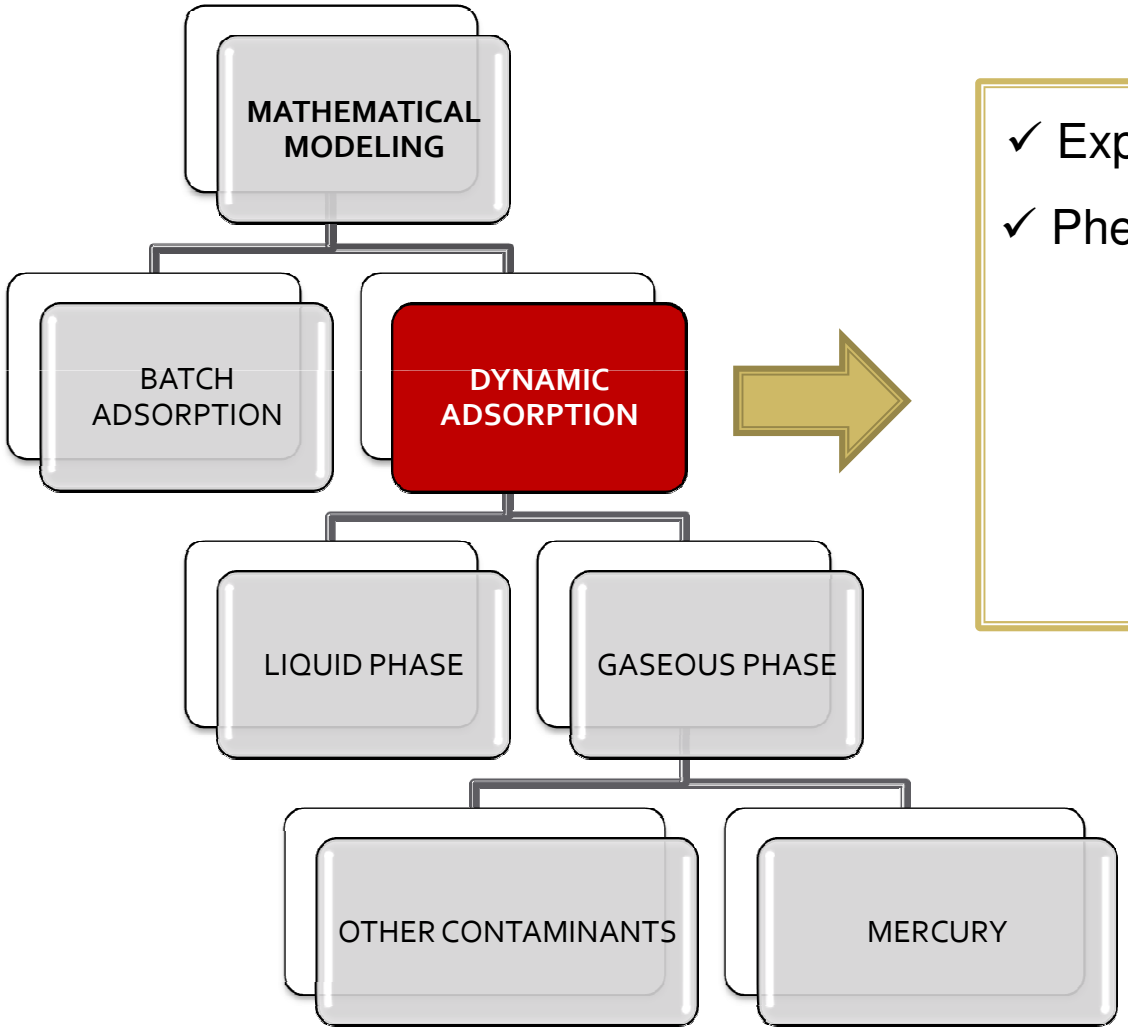
Modified HAp

HAp-M_xS_y

✓**Parameters:** Characteristics of adsorbent, bed length, inlet Hg concentration, flow rate

✓ **Long times to saturation**: low Hg concentrations and high Hg removal capacity

Combining Adsorption and Reaction Mechanisms



- ✓ Experimental breakthrough curves
- ✓ Phenomena
  - Advection
  - Axial diffusion
  - Diffusion into the particle
  - Adsorption

HIGH Hg FIXATION CAPACITY

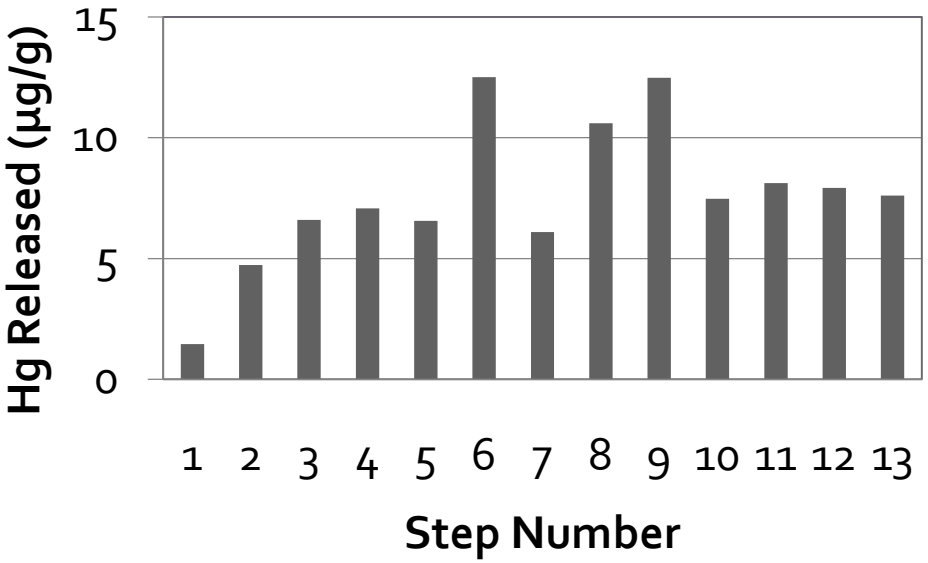
✓Addition of a **chemical reaction term** to classical adsorption models

Characterization of Used Sorbents

LIXIVIATION TESTS

-Suspension of samples in water (pH 5 at RT).

-Total time: 495 h (13 steps of 24, 70 or 95 h).

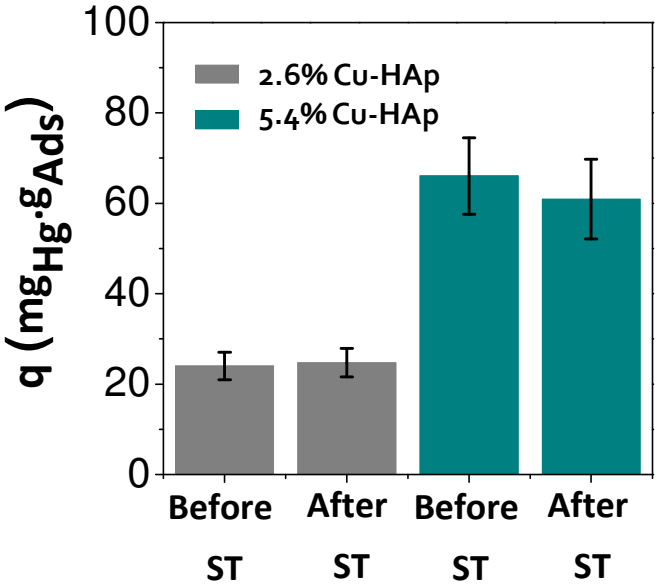


*Measurement: Cold Vapor AA (FIMS-400– Perkin-Elmer)

THERMAL STABILIZATION TESTS

- Exposition of samples to high temperatures

-Total time: 55 h (3 stages at 40, 60, 80 and 95ºC).

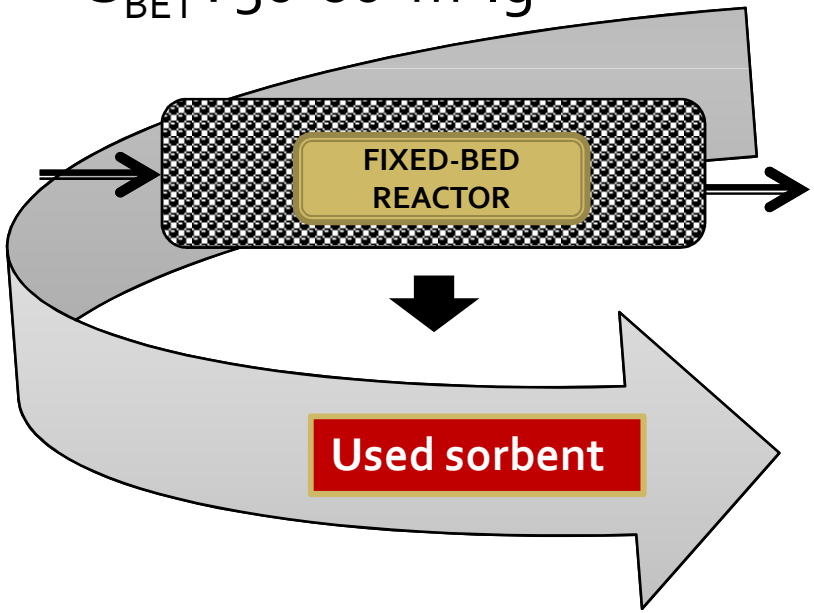


*Measurement: RA- 915+ (Lumex) (Differential Zeeman AA)

HIGH Hg FIXATION CAPACITY

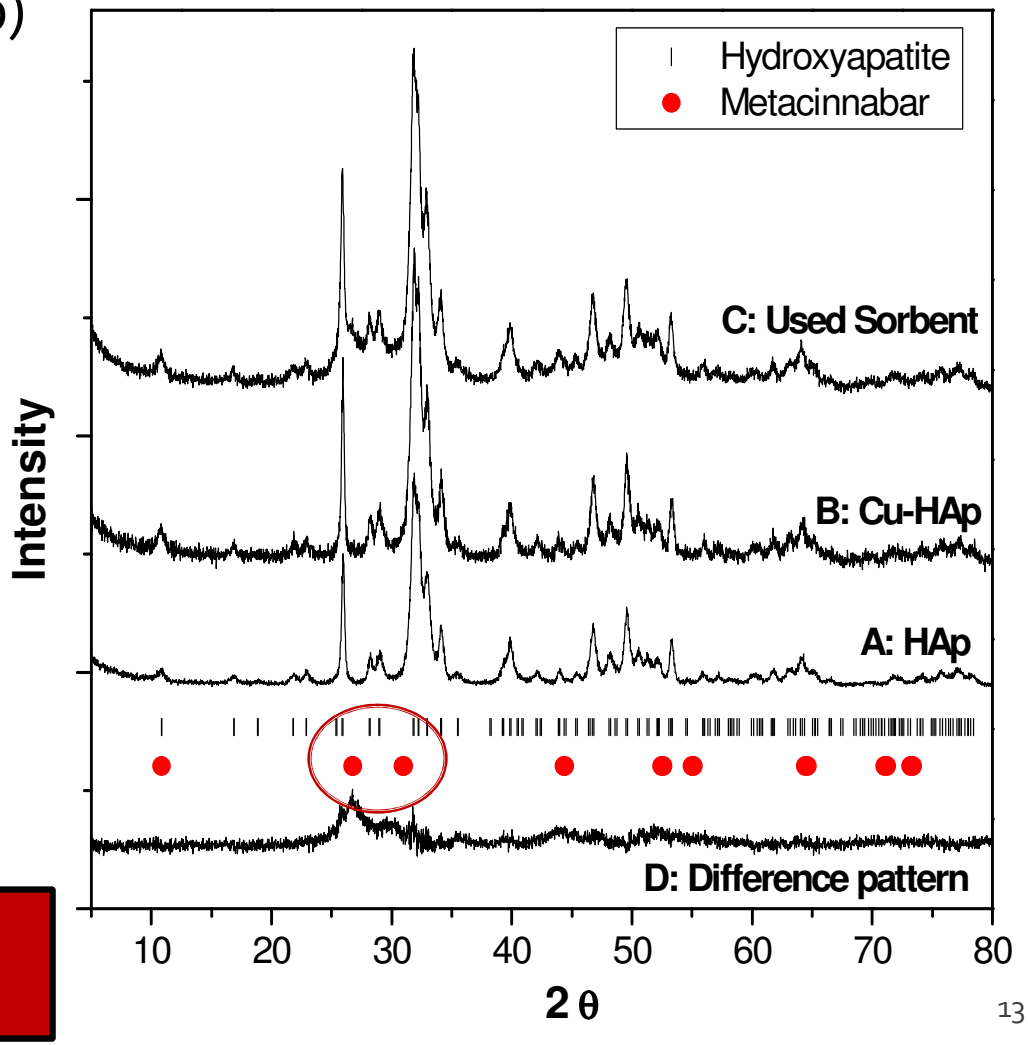
Sorbents Characterization

- ✓ Copper content: 1 - 7 % (p/p)
- ✓ Mesoporous particles
- ✓ S_{BET} : 30-80 $m^2.g^{-1}$



Formation of a stable phase
HgS

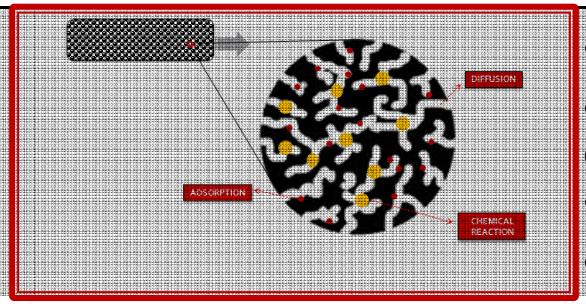
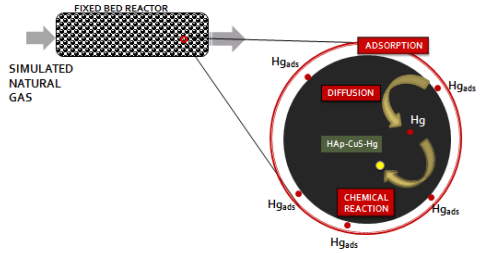
XRD results



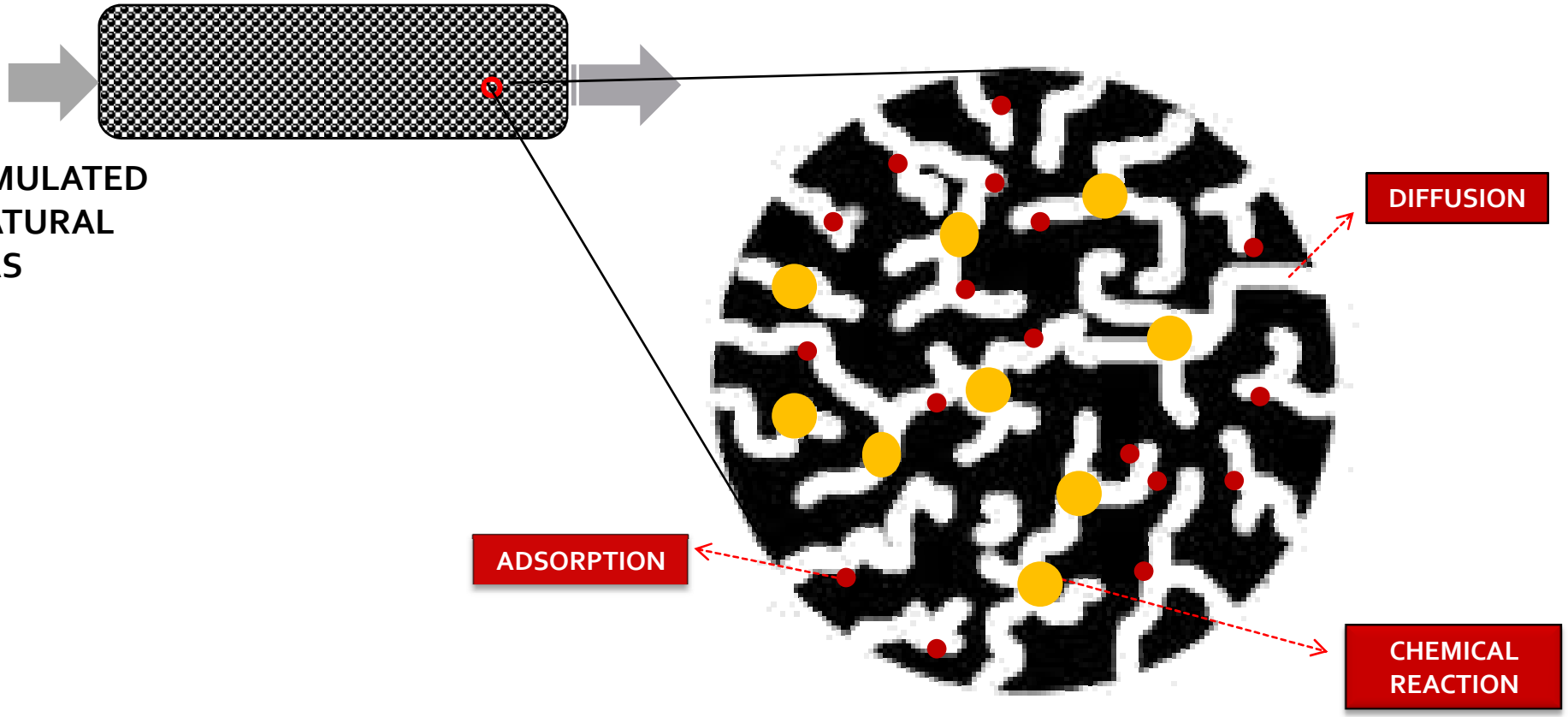
Summary of the Models

DYNAMIC MODELS TO Hg REMOVAL IN FIXED-BED REACTORS

- Mechanisms: Adsorption and Chemical reaction

Model	Flow pattern	Interface solid/fluid	Phenomena	Method of Solution	Software
1	**Axial** dispersion	**Kinetic** model		•**Bed:** Polynomial approximation in finite elements •**Particle**: Polynomial approximation	EMSO
2	**No** dispersion	**Linear Isotherm**		•**Bed:** finite difference •**Particle:** simplification by using parabolic profile to Hg concentration into the particle	Matlab

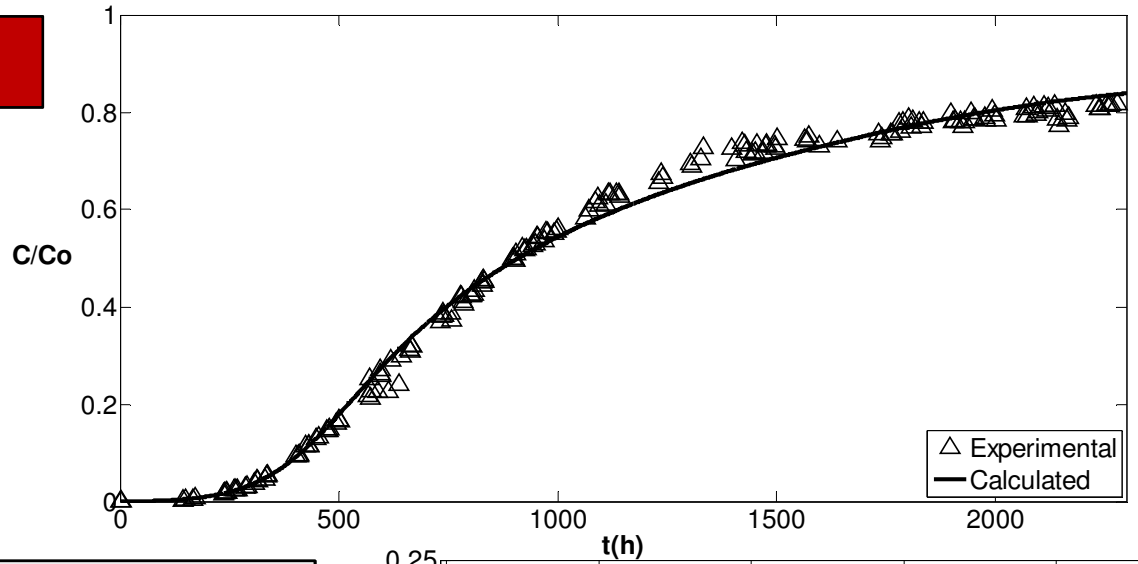
Model 1 : Assumptions



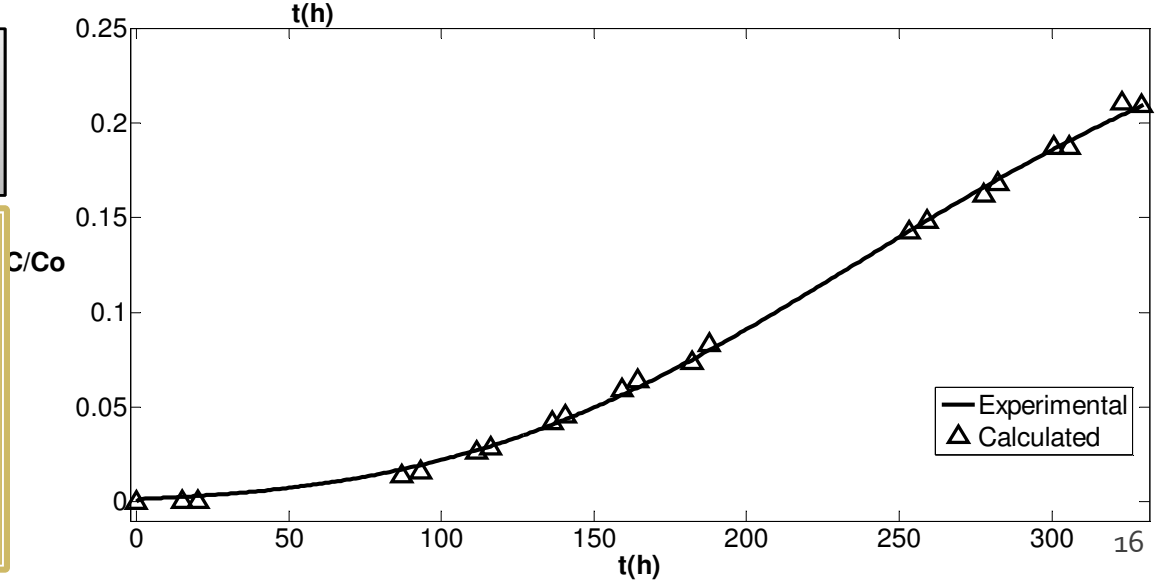
*Camargo, C.L.M., Oliveira, A.G., Resende, N.S., Biscaia Jr. E. C. , Secchi A. R. , Tavares, F.W., Salim, V.M.M., *In submission.*
Modeling of Hg° removal from gaseous streams and its fixation in hydroxyapatites-based adsorbents modified with copper sulfide

Model 1: Results

CASE 1



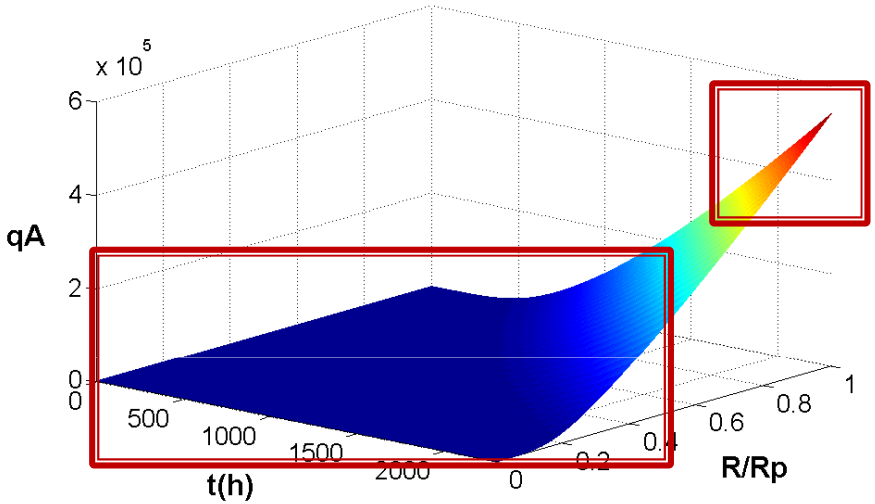
CASE 2

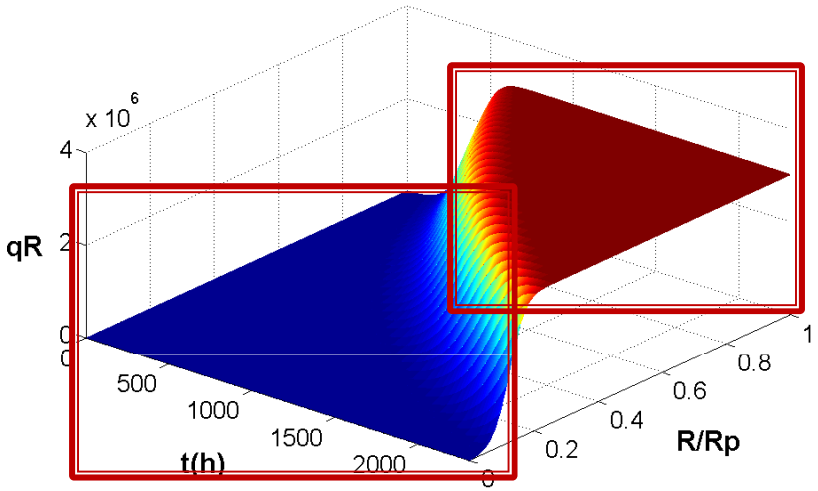


Different solids

Good agreement with both experimental data sets

Model 1: Results





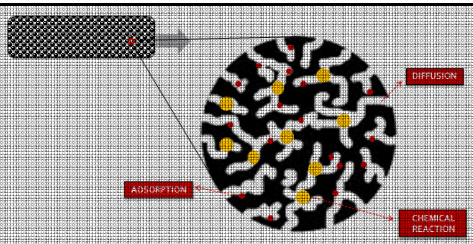
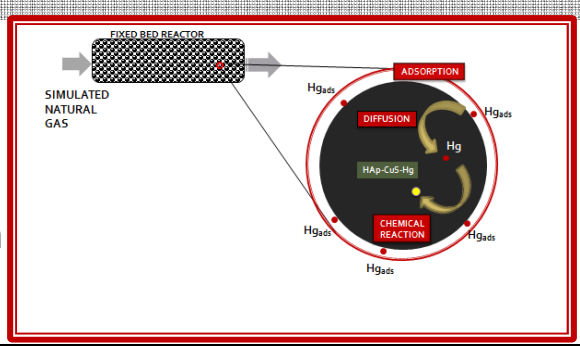
- ✓ The high availability of both sites: high removal capacity
- ✓ Chemical reaction wave advanced faster than the adsorption wave
- ✓ **Possibility: Location of sites should be into the sorbent matrix**

(delay in the waves because Hg needs to migrate into this matrix)

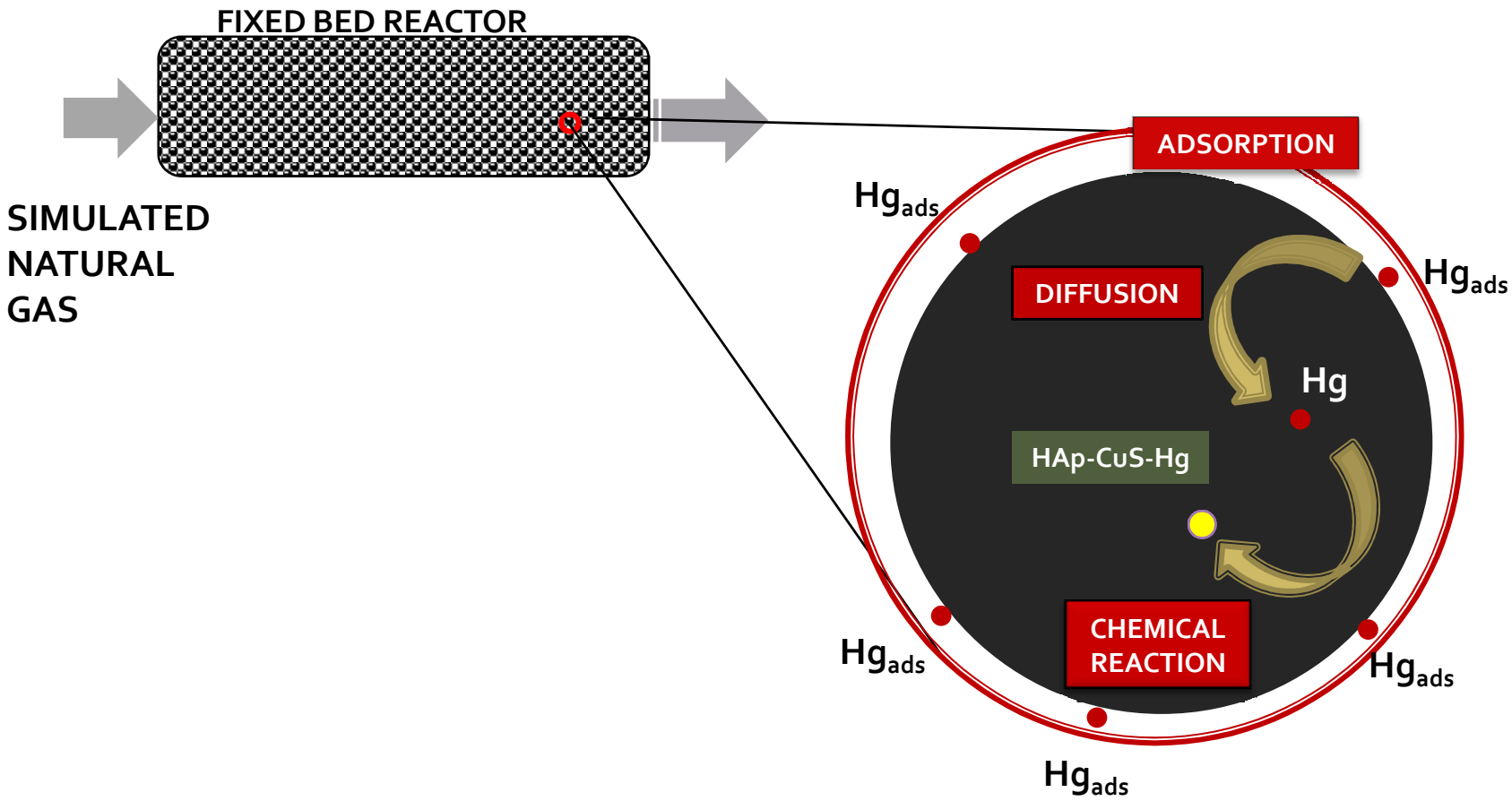
Summary of the Models

DYNAMIC MODELS TO Hg REMOVAL IN FIXED-BED REACTORS

- Mechanisms: Adsorption, Diffusion and Chemical reaction

Model	Flow pattern	Interface solid/fluid	Phenomena	Method of Solution	Software
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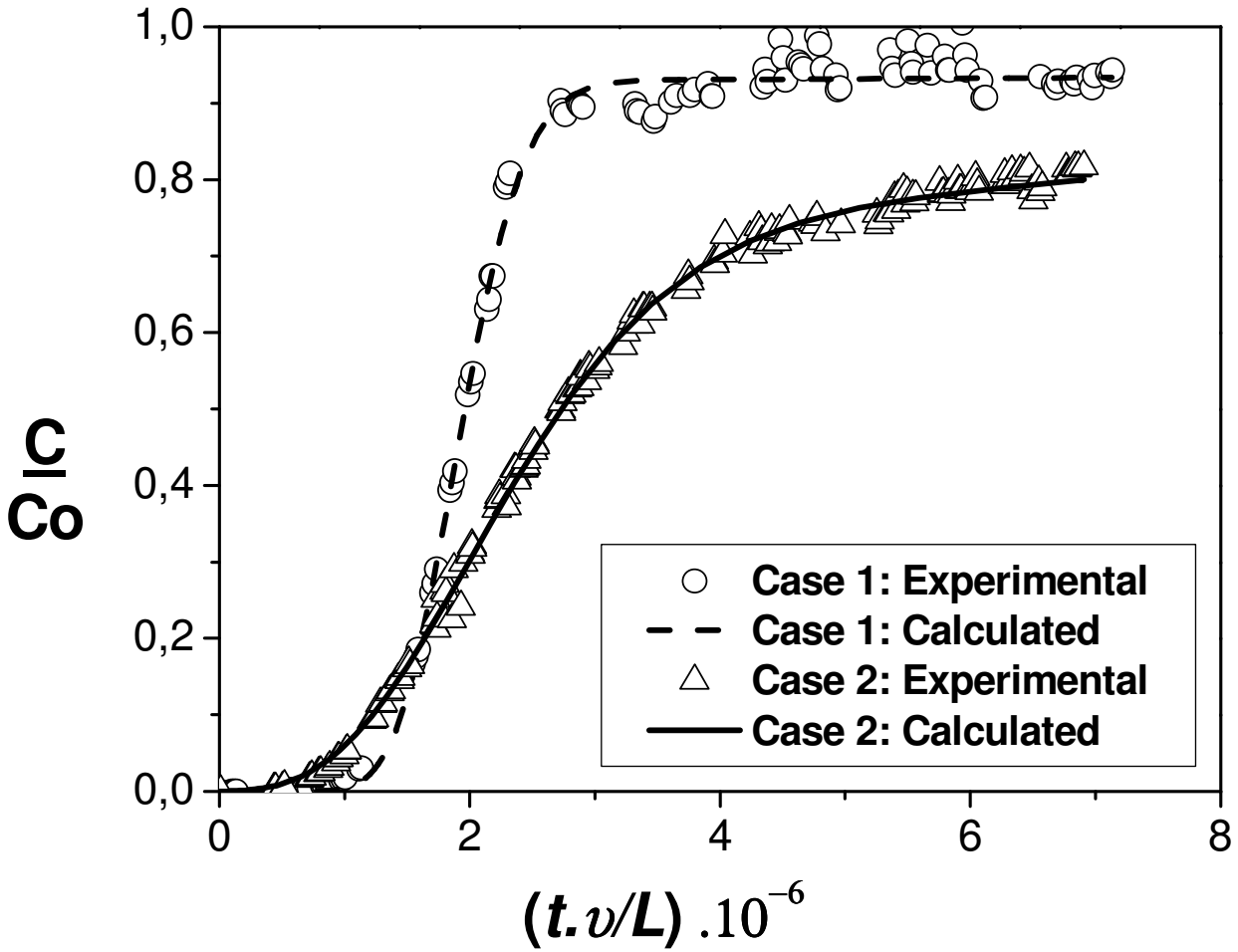
Model 2 : Assumptions



*Camargo, C.L.M., Resende, N.S., Oliveira, A.G., Salim, V.M.M., Tavares, F.W. (2014) *Fuel* **129**, 129.
Investigation of adsorption-enhanced reaction process of mercury removal from simulated natural gas by mathematical modeling

Model 2: Results

BREAKTHROUGH CURVES

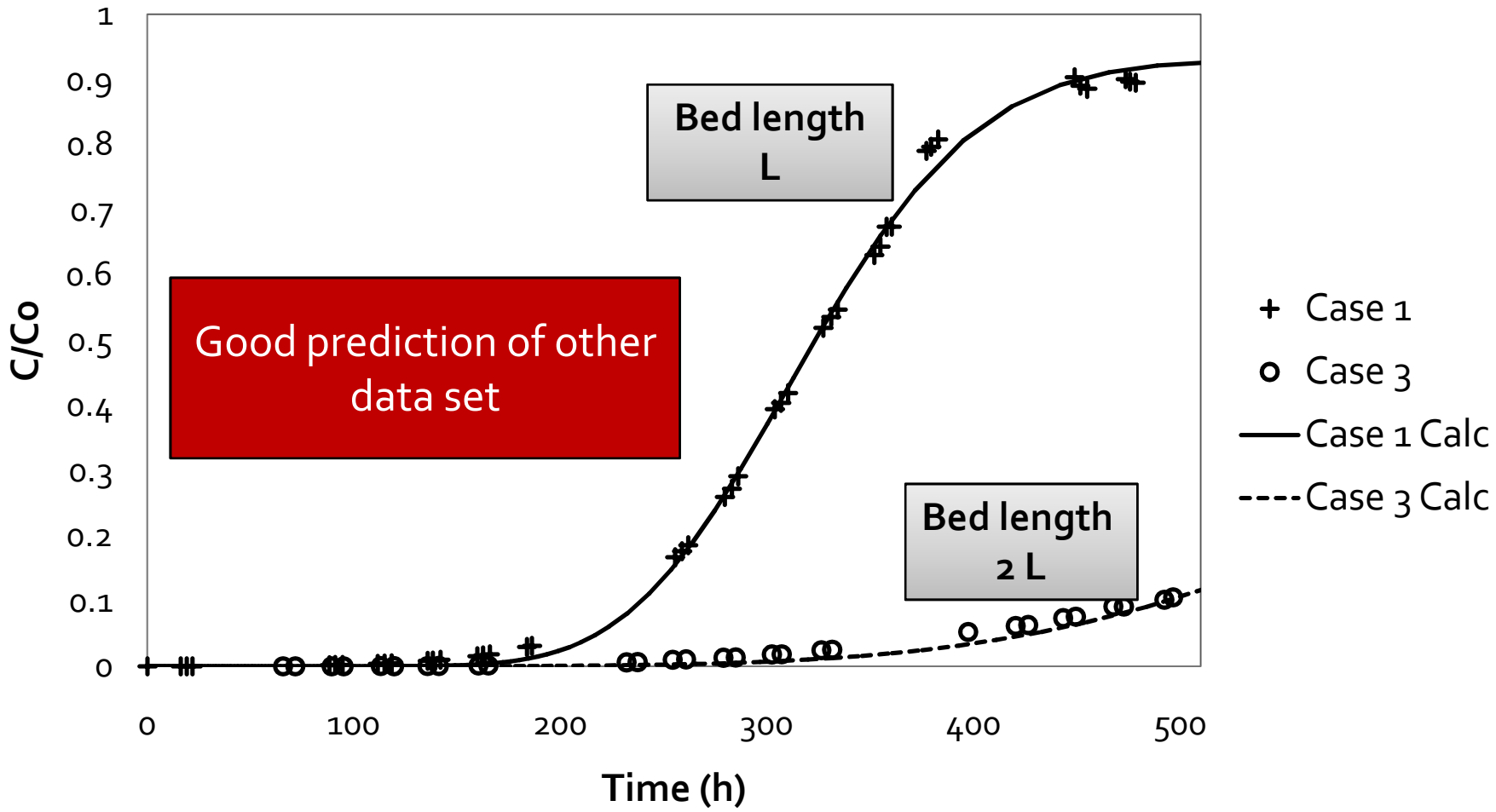


Different solids

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Model 2: Results

BREAKTHROUGH CURVES

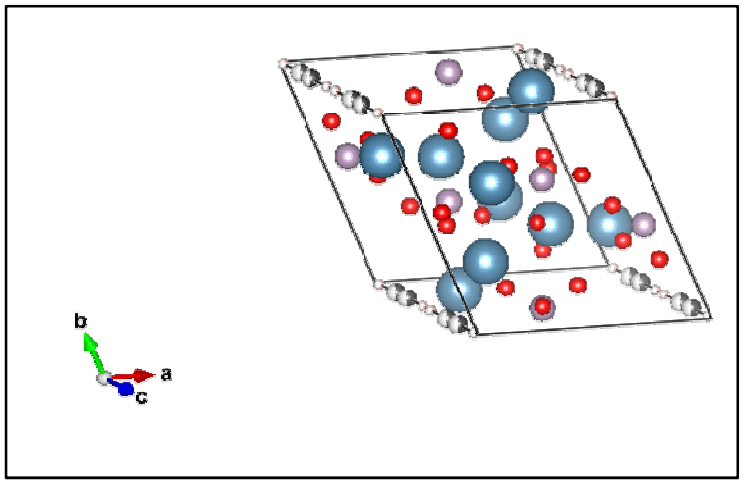


Remarks

- ✓ **Characteristics of HAp modified with copper sulfide sorbents:**
  - High efficiency to Hg^0 removal from NG streams
  - High removal capacity;
  - High fixation capacity.
- ✓ **Occurrence of chemical reaction (HgS)**
  - Supported by sorbent characterization and stabilization tests.
- ✓ **Models Results**
  - Good prediction of experimental results;
  - Indication of an adsorption-enhanced chemical reaction process.

Current challenges

Experimental techniques



✓Accurate study of crystal structures;

✓ Phase quantification.

-Rietveld Refinement

Computational techniques

✓Study of Hg diffusion into HAp crystalline matrix

- Molecular dynamics

- Software: *Lammps.*

✓ Use of experimental information.



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ATOMS



Federal University
Rio de Janeiro

Thank you for your attention!